

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 November 2001 (15.11.2001)

PCT

(10) International Publication Number
WO 01/85606 A1

(51) International Patent Classification⁷: **C01B 3/06, B01J 7/02, 8/02**

(21) International Application Number: **PCT/CA01/00682**

(22) International Filing Date: **14 May 2001 (14.05.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
2,308,514 12 May 2000 (12.05.2000) CA

(71) Applicant (*for all designated States except US*): **MCGILL UNIVERSITY [CA/CA]; 845 Sherbrooke Street West, Montreal, Québec H3A 1B1 (CA).**

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **ZALUSKI, Leszek [CA/CA]; 3510 Paule-Emile Cote, Montreal, Québec H4E 1Z6 (CA). ZALUSKA, Alicja [CA/CA]; 3510 Paul-Emile-Cote, Montreal, Québec H4E 1Z6 (CA). STROM-OLSEN, John, Olaf [CA/CA]; 443 Lansdowne Avenue, Westmount, Québec H3Y 2V2 (CA).**

(74) Agents: **SWABEY OGILVY RENAULT et al.; 1981 McGill College Avenue, Suite 1600, Montreal, Québec H3A 2Y3 (CA).**

(81) Designated States (*national*): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.**

(84) Designated States (*regional*): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**

Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/85606 A1

(54) Title: **METHOD OF HYDROGEN GENERATION FOR FUEL CELL APPLICATIONS AND A HYDROGEN-GENERATING SYSTEM**

(57) Abstract: **Hydrogen is generated by reaction of a metal hydride and at least one alcohol which may be employed in conjunction with water; this provides a convenient, efficient method of generating hydrogen for a fuel cell.**

METHOD OF HYDROGEN GENERATION FOR FUEL CELL APPLICATIONS AND A HYDROGEN-GENERATING SYSTEM

5 TECHNICAL FIELD

The invention discloses a method of generating hydrogen for fuel cell applications, based on a chemical reaction of metal hydrides with alcohols, the invention also relates to a hydrogen generator using such reaction is described.

10 BACKGROUND ART

Fuel cells require a continuous supply of hydrogen and oxygen to produce electricity. At present however, storage and supply of hydrogen is the main 15 limiting step in the use of fuel cell systems. For vehicular applications, large amounts of hydrogen, typically of the order of several kilograms, are needed on-board between refuelling. However, current methods of hydrogen storage not only cannot provide sufficient hydrogen capacity, or volumetric density, to compete with gasoline cars, but have additional serious limitations. For example, 20 compressed hydrogen tanks operate at very high hydrogen pressure, typically 350 – 700 atm and so have a serious safety problem. Liquid hydrogen on the other hand needs cryogenic temperatures, typically about ten to fifteen degrees above absolute zero, and therefore requires costly and demanding cryogenic equipment. In the case of miniature fuel cells for portable applications, for 25 example for laptops or cellular phones, the hydrogen storage is even more critical, because both of these storage methods are totally impractical on the small scale.

Metal hydrides offer a good solution for hydrogen storage: they are safe, stable and provide indefinite storage without hydrogen loss. In general, the use of 30 metal hydrides is based on the reversible cycling of hydrogen absorption and desorption under certain pressure/temperature conditions. A variety of metal hydrides is known, having various hydrogen capacities and different pressure/temperature characteristics.

In general, metal hydrides can be divided into two groups:

a) "unstable" hydrides operating at room temperature. These hydrides require hydrogen pressure, typically between 2 and 5 atm, to be maintained in the tank, otherwise the hydrogen is immediately released from the hydride. These room-temperature hydrides, for example those based on LaNi₅ or FeTi,
5 provide easy and fast hydrogen desorption, but have low hydrogen storage by weight, typically around 1 wt.%.

b) "stable" hydrides operating at elevated temperatures. These metal hydrides can indefinitely store hydrogen at room temperature, even without
10 hydrogen overpressure. However, desorption requires raising the temperature, in some cases significantly. For example, Mg-based hydrides need to be heated to temperatures close to 300°C in order to release hydrogen. Although these hydrides have high hydrogen capacities, reaching 7.6 wt.% in the case of MgH₂, the high temperature of hydrogen desorption is a serious practical disadvantage.
15

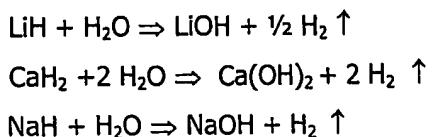
Very few metal hydrides are known where thermodynamic properties allow reversible operation at moderate temperature, such as temperatures below or around 100°C, and also having good hydrogen capacity. One example is NaAlH₄, which can operate reversibly with good kinetics and hydrogen capacity of 5.6
20 wt.%, but only after advanced catalysis [1,2]. However, currently even catalyzed NaAlH₄ becomes impractically slow at temperatures below 100°C, which is required for the PEM fuel cell applications.

An alternative method for generating hydrogen from these stable hydrides
25 without the need to raise the temperature is through a chemical reaction leading to the decomposition of the hydride. For example, water may be used to release hydrogen via hydrolysis reaction. Water reacts with certain metal hydrides, forming hydroxides and the release of gaseous hydrogen.
Hydrolysis has been used in a series of hydrogen generators. For example, U.S.
30 Pat. 4,155,712 [3] discloses a small generator containing metal hydride which produces hydrogen in the reaction with water vapor. Another U.S. Pat. 4,356,163

[4] discloses utilizing a chemical reaction of an alkali metal with water for the hydrogen generation.

Examples of the hydrolysis reaction are as follows:

5



10 Generation of hydrogen by a hydrolysis reaction is effective, but has disadvantages. One is that hydrolysis reactions are usually violent and generate large amounts of heat. Once started, they are extremely difficult to control and may proceed in an explosive manner. For example, in the case of LiAlH_4 , the heat of hydrolysis causes a very rapid increase of temperature, which results in an instant thermal decomposition of the hydride, so that the reaction cannot be controlled by simply limiting the amount of water, and proceeds rapidly once initiated. One way around this is to immerse the hydride in a mineral oil [5], which makes the reaction more controllable. This however reduces the effective hydrogen capacity at least by half, because the oil-based slurry needs to contain 15 about 50 wt.% of the mineral oil. Another method to avoid explosive reaction is disclosed in U.S. Patent 5,593,640 [6], where a combination of adiabatic hydrolysis and thermal decomposition is claimed to provide a controllable generation of hydrogen. In this generator, LiAlH_4 is allowed to undergo hydrolysis only at temperatures exceeding the temperature of the initiation of 20 thermal decomposition, which is effected by heating the hydride before hydrolysis in a complex generator.

25 The use of sodium hydride instead of lithium hydrides results in a less violent reaction, but at the expense of hydrogen capacity, which is reduced simply because sodium is much heavier than lithium. A hydrogen generator based on 30 the hydrolysis of sodium hydride is disclosed in U.S. Patents 5,728,464 and 5,817,157 [7,8]. This reaction has however another disadvantage. It requires a significant excess of water, because the reaction product, sodium hydroxide,

causes solidification of the solution when its content exceeds 50 mol%, thus stalling any further hydrolysis.

Among other hydrides, NaBH_4 reacts with water only when specially catalysed, for example by a special Ru-based catalyst [9]. In this case however, the same 5 problems as with NaH occur, namely precipitation of the solid reaction product, NaBO_2 , which requires the NaBH_4 solution to be diluted to 20 mol% of NaBH_4 and thus results in reduced hydrogen capacity. Another technical problem is that controlling the reaction can be done only by either immersing the catalyst in the solution, which promotes the reaction or by completely removing the catalyst 10 from the solution, which stops the reaction, so that intermediate reaction rates are not accessible. In another design of the hydrogen generator it was pointed out that for portable applications the heat of hydrolysis of NaBH_4 , LiBH_4 , LiAlH_4 or NaAlH_3 is so large that the hydrolysis-based generators could be too hot to be practical. In these cases the heat of hydrolysis is used to generate steam for the 15 steam-hydrolysis of the hydrides [10].

All hydrolysis reactions have also one common problem: the use of water limits the temperature range of the hydrogen generator to temperatures above 0°C, to 20 avoid freezing of the water. This is a serious limitation for the outdoor use of the hydrolysis-based generators in a cold climate, which may require a "cold start-up" at temperatures below -20°C, or even -40°C.

Thus at present, none of the above methods of storing and generating 25 hydrogen represents a fully efficient, safe and reliable source of hydrogen for fuel cells. All the above methods suffer from serious limitations and therefore alternative methods of hydrogen generation are needed. It is the aim of the present invention to offer such an alternative method.

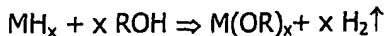
DISCLOSURE OF THE INVENTION

5 In accordance with one aspect of the invention there is provided a process for generating hydrogen from a metal hydride comprising: reacting a metal hydride with at least one alcohol.

10 In accordance with another aspect of the invention there is provided a hydrogen generator comprising: a) a first housing containing a metal hydride; b) a second housing containing at least one alcohol for reaction with said metal hydride, c) flow means for delivery of said at least one alcohol from said second housing to said first housing, and d) hydrogen gas outlet means in said first housing for delivery of generated hydrogen gas from said first housing.

15 **DETAILED DESCRIPTION OF THE INVENTION
AND DESCRIPTION OF PREFERRED EMBODIMENTS**

The present invention relates to a new method of hydrogen generation particularly for fuel cell applications. In this method, hydrogen is produced from a metal hydride in a chemical reaction with an alcohol. The metal hydride may 20 be a simple metal hydride or a complex metal hydride. In the case of a simple metal hydride the reaction proceeds by the following generic reaction which is the basis for the hydrogen production:



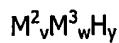
25 in which MH_x is a simple metal hydride and ROH is an alcohol. In the above metal hydride M is, by way of example, typically Li, Na, K, Mg, Ca, Be, Sr, K, Nb, Zr or Ti; R is typically an alkyl group of 1 to 10, preferably 1 to 6 and more preferably 1 to 4 carbon atoms, for example, methyl, ethyl, n-propyl, iso-propyl, 30 n-butyl, sec.butyl or tert.butyl. The designation x is an integer typically of 1 to 4.

In this reaction, the metal atom (M) from the hydride substitutes hydrogen in the hydroxyl group (OH) in the alcohol. As a result, another compound is formed,

namely, an alkoxide, and hydrogen is released from the metal hydride and, from the alcohol.

The above exemplification of the process is made for ease of description for the case of a simple metal hydride; however, the hydrogen generation proceeds 5 similarly with complex metal hydrides and with mixtures of simple and complex metal hydrides.

By way of example, complex metal hydrides which may be employed in the invention include those of formula:



10 in which M^2 is metal selected from the group consisting of Li, Na, K, Mg, Ca, Fe and Zr; M^3 is selected from the group consisting of Al, B, Be and Ti; v is an integer of 1 to 3; w is an integer of 1 to 3; and y is an integer of 4 to 8.

However, the invention extends to all metal hydrides and is not confined to the particular subclasses of metal hydride or specific metal hydrides referred to in 15 the illustration of the invention herein.

By way of example metal hydrides for use in the invention include simple alkali metal hydrides such as LiH, NaH, KH, RbH, CsH, hydrides of the elements of main group II metal BeH₂, MgH₂, CaH₂, SrH₂, BaH₂, metallic-type hydrides e.g. ScH₂, YH₂, YH₃, TiH₂, ZrH₂, HfH₂, VH, VH₂, NbH, NbH₂, TaH, PdH, 20 rare earth hydrides e.g. LaH₂, CeH₂, PrH₂, NdH₂, SmH₂, GdH₂, DyH₂, TbH₂ covalent hydrides e.g. CuH, ZnH₂, AlH₃, GaH₃, InH₃, ThH₃, SnH₄, PbH₄ and boranes, silanes and germanes, + mixed (complex) hydrides of the above elements, e.g. ternary etc, for example LiAlH₄, (Li-Na)AlH₄, LiBH₄, NaBH₄, KBH₄, and their non-stoichiometric hydrides and solid solutions.

25 Metal hydrides have been found to readily react with alcohols, for example with methanol, ethanol or higher alcohols, and the reaction produces a steady and abundant flow of hydrogen at room temperature and below.

Thus the invention has the advantage that the process proceeds conveniently at 30 temperature below 30°C, preferably below 25°C and 20°C and below. Moreover, the amount of the hydrogen released is greater than that obtained from the thermal decomposition of the hydride, because hydrogen comes not only from the hydride, but also from the hydroxyl group of the alcohol.

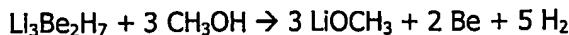
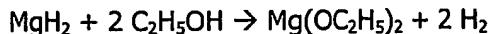
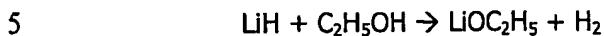
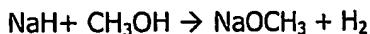
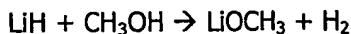
Table I summarizes nominal hydrogen capacities obtained from various metal hydrides in the alcoholysis reaction of the invention. The hydrogen capacities are given in wt % with respect to the weight of the hydride, and also in hydrogen volume obtained in the alcoholysis reaction from 1 kilogram of the hydride. Total 5 hydrogen capacities, including both the weight of the hydride and weight of alcohol are also listed. Although in some reactions an excess of alcohol is advantageous for the reaction rate, the alcohol excess was not taken into account in the Table. It should be noted here that in the case of more complex reactions, for example involving bi-metallic hydrides (i.e. with two different metal 10 atoms) the overall hydrogen capacities are dependent on the reaction route and may change depending on the applied temperature, catalysis and excess of the alcohol.

TABLE I

Hydride	wt. % of H ₂ (in respect to the hydride weight)	Litres of H ₂ obtained per 1 kg of hydride	Total H ₂ capacity (including the weight of the hydride and the alcohol - methanol)
LiH	25.4	2845	5.0
LiAlH ₄	13.2	1478	7.2
Li ₃ AlH ₆	16.8	1882	6.1
LiBH ₄	23.1	2592	9.4
NaH	8.3	933	3.6
NaAlH ₄	9.3	1045	5.9
Na ₃ AlH ₆	8.9	996	4.6
NaBH ₄	13.3	1490	7.3
Li ₃ Be ₂ H ₇	22.0	2460	7.1
Li ₂ BeH ₄	22.5	2516	6.7
MgH ₂	15.3	1716	4.5
CaH ₂	9.6	1074	3.8
FeTiH ₂	5.7	641	2.6
ZrH ₂	4.3	484	2.6
TiH ₂	8.1	905	3.5
MgAl ₂ H ₈	11.7	1307	6.7
LiAl ₂ H ₇	11.9	1329	8.1
ZrAl ₂ H ₈	6.6	737	4.6

- 9 -

Examples of the specific reactions of hydrogen generation are as follows:



According to these reactions, metal hydrides produce alkoxides and hydrogen in
10 the reaction with alcohols. Metal alkoxides are derivatives of alcohols (MOR) and
constitute an important branch of organometallic chemistry. The research on
alkoxides was initiated more than a century ago and now alkoxides find a variety
of important applications, for example as drying agents, water-repellents, and
paint components. The most common catalytic applications of alkoxides include
15 redox catalysis and olefin polymerization catalysis. Alkoxides are also used as
precursors to metal oxides. High purity oxides can be obtained through
hydrolysis, pyrolysis or combustion of alkoxides. Metal alkoxides are usually
produced by one of the following methods (as widely described for example in a
review book "Metal alkoxides" [11]):

20

- reaction of metals with alcohols
- reaction of metal halides with alcohols
- reaction of metal hydroxides and oxides with alcohols
- alcohol interchange
- transesterification reactions

25

- reactions of metal dialkylamides with alcohols.

Although alkoxides can be effectively produced by all these techniques and most
of the above methods are used on an industrial scale, the formation of alkoxides
from hydrides has been never considered in practice probably for a number of
30 reasons. First, the hydrides now found to be very efficient in the generation of
hydrogen in the alcoholysis reactions, were previously either very difficult to
fabricate, as for example Mg hydride, or Na₃AlH₆, or not known, for example Li-

- 10 -

Be hydrides, or (Li-Na)-Al hydrides. Only recent advances in metal hydrides synthesis by solid-state reactions enabled easy fabrication of many hydrides [13]. Another reason not to consider formation of alkoxides from hydrides, especially when the use of metals is sufficiently effective, is that the release of 5 hydrogen from the hydride could be a serious complication during the alkoxide production. This potentially negative feature of the alcoholysis reaction is the key of the hydrogen generation in the present invention.

As seen in Table 1, various hydrides can be used for the hydrogen production, 10 and the optimum hydride can be chosen based on the required hydrogen capacity, the hydride cost and the required reaction rate.

Methanol, CH_3OH is the simplest and the lightest of all alcohols, therefore alcoholysis of metal hydrides with methanol gives the highest total hydrogen capacity, as shown in the Table. However, ethanol or higher alcohols provide 15 much better reactivity with certain hydrides, for example complex borohydrides or calcium hydride CaH_2 . The type of alcohol in the hydrogen generator can be chosen depending on the metal hydride, and also on the required reaction route and kinetics. Since alcohols are easily mixable, a mixture of two or more alcohols can be used in a very wide proportion. For example, a mixture of methanol and 20 ethanol can be used, where methanol provides higher overall hydrogen capacity and ethanol better reactivity. The appropriate proportion of methanol/ethanol mixture can be adjusted during the efficiency testing of the hydrogen generation.

25 As mentioned above, the crucial advantage of the alcoholysis reaction over the hydrolysis reaction, is the potential of operating at temperatures below the freezing temperature of water. Even more convenient however is to use a mixture of alcohol and water, a common "windshield fluid", to produce hydrogen. In this case, the reaction is a combination of alcoholysis and 30 hydrolysis, with two great enhancements over the hydrolysis alone: a more controllable reaction rate and possible operation at temperatures much below 0°C. The main advantage of the hydrogen generator based on the combined

hydrolysis and alcoholysis is its flexibility to the "reactive liquid" used. The "reactive liquid", i.e. the mixture of alcohol, or alcohols, with water can be adjusted depending on the climate or season, with a higher proportion of alcohol in the liquid when operating at lower temperatures is required, and with more 5 water when more rapid hydrogen desorption is needed.

In certain cases, as for example in the case of alkali metal borohydrides, for example, LiBH_4 and NaBH_4 , the alcoholysis reaction needs to be catalyzed in order to increase the reaction rate. The addition of a solid-state catalyst can be very efficient in enhancing the reaction kinetics. Various catalysts can be used 10 for this purpose, depending on the metal hydride and on the alcohol, for example iodine and its compounds, chlorides, or various metals, e.g. Ru, Ni, Ti and Fe and their compounds. The catalyst can be introduced either in the solid state, admixed to the hydride, or in a solution with alcohol, or dissolved in another, neutral solvent.

15 A single type of hydride can be used in the hydrogen generator, but in some cases a mixture of two or more hydrides can be more advantageous. The main reason for using a mixture of hydrides is modification of the reaction rate or catalysis. Usually there is no inter-reaction in the mixture of two hydrides in the 20 powdered form at room temperature. However, when the mixture is immersed in alcohol, the reaction route, and the reaction rate, can be completely changed, as compared to the two hydrides alone. This can be effected by either formation of hetero-alkoxides, or by a combined, synergetic reaction, where the more reactive component induces the reaction of the "slower" component. This can be 25 particularly advantageous when the slow hydride is inexpensive and has high hydrogen capacity, and the fast hydride is more expensive or difficult to fabricate. The fast reaction can induce and promote the second reaction in a synergetic way, as shown for example for hydrogen desorption in a mixture of MgH_2 and Mg_2NiH_4 [13].

30 Usually the most convenient form for the hydride, or hydrides, inside the generator before adding alcohol, or its mixture with water, is in the solid state, typically in a powdered form. However, when a fast refilling of the hydride

- 12 -

container is required, the hydride may be contained in a neutral solvent, for example tetrahydrofuran or toluene, and so easily pumped into the tank.

The alcohol may be in liquid, gaseous or vapor state.

5

As described above, the alcoholysis reaction of metal hydrides leads to the formation of metal alkoxides. There are two ways of dealing with the reaction products, i.e. recovering the metals. In some cases, simple hydrolysis or pyrolysis of the alkoxides gives a very valuable oxide product of very high purity 10 and dispersion, which is ideal for many catalytic applications. An example is magnesium oxide, zirconium oxide or titanium oxide. Alkali metals in contrast, form hydroxides, for example LiOH or NaOH, as a result of hydrolysis of the respective alkoxides, which can be subsequently thermally decomposed into lithium and sodium hydrides and returned into the hydrogen generator.

15

In a typical reduction to practice, the metal hydride, or a mixture of two or more hydrides, is allowed to react with alcohol simply by pouring or injecting the alcohol into the hydride container. As a result of the alcoholysis reaction, hydrogen gas is released. Hydrogen is directed toward a fuel cell system. 20 Controlling the supply of alcohol, or a mixture of alcohol and water, can easily control the rate of reaction and the release of hydrogen. Gradual feeding with the "reactive liquid" regulates the amount of the produced hydrogen, and the reaction can be thus stopped or increased depending on the demand for hydrogen. In a practical way it is effected through an injection system, which 25 reduces the supply of the "reactive liquid" in response to the increasing pressure of the produced hydrogen.

The invention also relates to a hydrogen generator as described hereinbefore. A typical hydrogen generator may have the following features or components:

- 13 -

1. A container with metal hydride, preferably being in a powder form, or in a solution in a neutral liquid. The container can consist of a single reaction chamber, but for large-scale application several separate reaction chambers can be more advantageous in order to have better control of the reaction.
2. A container with the "reactive liquid", e.g. the alcohol, a mixture of alcohols or a mixture of alcohol with water.
3. An injection system with a regulator for the controlled supply of the "reactive liquid" to the metal hydride.
4. A hydrogen outlet towards the fuel cell system, with pressure controller and safety gauge.

The above hydrogen generator can be used either as a main source of hydrogen for fuel cells, or as a start-up device only. In the latter case, the main hydrogen supply can be provided for example by thermal decomposition of metal hydrides.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a schematic representation of a hydrogen generator of the invention.

20

DETAILED DESCRIPTION OF DRAWINGS

With further reference to Fig. 1, a hydrogen generator 10 comprises a container 12 for metal hydride, a container 14 for a reservoir of an alcohol, a hydrogen collection tank 16 and a hydrogen outlet conduit 18.

25

Container 12 as illustrated is modular having a plurality of discrete and separate compartments 20 for metal hydride. A feed conduit 22 connects the container 14 with a selected compartment 20.

30 Included in feed conduit 22 is a heater/cooler 24, as an optional component, a feed injector 26 and a valve 28 which controls the feed of the alcohol to the selected compartment 20.

A conduit 30 having a valve 32 communicates container 12 with tank 16; a valve 34 is disposed in hydrogen outlet conduit 18.

- 5 In operation an alcohol or a mixture of alcohols or an aqueous alcohol or alcohol mixture is injected from container 14 to a selected compartment 20, optionally with heating or cooling in heater/cooler 24. The alcohol or other reactive alcohol mixture, with the metal hydride in the selected compartment 20 of container 12 with generation of hydrogen gas which flows from container 12 to tank 16.
- 10 Hydrogen is delivered from tank 16 via conduit 18 as required, for example, to a hydrogen fuel cell.

When the selected compartment is depleted in the metal hydride the modular compartment 20 may be replaced by a new compartment having a fresh supply 15 of metal hydride. The metal alkoxide by-product may be recovered from the exchanged modular compartment.

Although the above reactions of alcohols with metal hydrides are aimed mainly towards the generation of hydrogen, they may actually also open the door to 20 better ways for the formation of various metal alkoxides. In certain cases, complex alkoxides cannot be produced by a simple alcoholysis of metals or other compounds and the reaction with the respective hydride is the only way to produce these new alkoxides. An outstanding example is a newly synthesized Li₃Be₂H₇ hydride. In the dehydrogenated form the material simply consists of a 25 mixture of two immiscible metals: Li and Be. In the hydrogenated state however, hydrogen atoms bond Li and Be together, forming a hydride. Therefore, the alcoholysis reaction with the Li₃Be₂H₇ is different (under certain experimental conditions) than that with Li and Be alone, and therefore more complex compounds can be formed: bi-metallic alkoxides i.e. containing two different 30 metal atoms. This reaction was only possible after an efficient method of the hydride formation was developed, as described in reference [14]. Other "double" hydrides (for example LaNi₅H₆, FeTiH₂ or Mg₂NiH₄) also offer the possibility of

- 15 -

producing unique, double alkoxides, for which this reaction path was never considered before.

In a particular embodiment the method employs a combination of an alcohol and
5 water, this combination gives the following advantages:

- maximization of the hydrogen production (because both reactions fully contribute to the hydrogen generation)
- fully controllable reaction rate (and route) through the adjustable
10 contribution of the two reactions in the process (by the alcohol-to-water ratio)

For example, the normally "explosive" hydrolysis of LiAlH_4 can be tamed and controlled by the addition of alcohol, without sacrificing the hydrogen capacity

- Certain hydrides, for example borohydrides do not undergo hydrolysis without special catalysis, but the addition of alcohol can change their activity (or reaction route) in such a way, that hydrogen generation may proceed effectively, without the loss of hydrogen capacity
- The use of combined alcoholysis and hydrolysis extends the temperature range of the hydrogen production towards temperatures below freezing
20 temperature of water.

References:

1. "Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials" B. Bogdanovic, M. Schwickardt, J. Alloys Comp. 253 (1997) 1
2. "Sodium alanates for reversible hydrogen storage" A. Zaluska, L. Zaluski and J.O. Ström-Olsen, J. Alloys Comp. 298 (2000) 125
- 30 3. "Miniature hydrogen generator", W.G. Taschek, U.S. Pat. No: 4,155,712
4. "Process for the production of hydrogen", J.G. Davidson, U.S. Pat. No 4,356,163

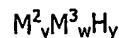
- 16 -

5. "Hydrogen transmission/storage with a chemical hydride/organic slurry"
R. Breault, Proceedings of 9th Canadian Hydrogen Conference,
Vancouver, BC, Canada 1999, 393
6. "Portable hydrogen generator" E. Long, J. Schmidt and F. Lynch, U.S.
5 Patent No 5,593,640
7. "Hydrogen generation system and pelletized fuel" J.H. Checketts, U.S.
Patent No 5,728,464
8. "Hydrogen generation system and pelletized fuel" J.H. Checketts, US
10 Patent No 5,817,157
9. "An ultrasafe hydrogen generator: aqueous, alkaline borohydride
solutions and Ru catalyst" S.C. Amendola, S.L. Sharp-Goldman, M.S.
Janjua, M.T. Kelly, P.J. Petillo and M. Binder, Journal of Power Sources
85 (2000) 186
10. "Production of hydrogen from chemical hydrides via hydrolysis with
15 steam" R. Aiello, J.H. Sharp, M.A. Matthews, International Journal of
Hydrogen Energy 24 (1999) 1123
11. "Metal alkoxides" D.C. Bradley, R.C. Mehrotra and D.P. Gaur, Academic
Press, London, 1979
12. "Hydrogenation properties of complex alkali metal hydrides fabricated by
20 mechano-chemical synthesis" L. Zaluski, A. Zaluska, and J.O. Ström-
Olsen, J. Alloys Comp. 290 (1999) 71
13. "Synergy of hydrogen sorption in ball-milled hydrides of Mg and Mg₂Ni"
A. Zaluska, L. Zaluski and J.O. Ström-Olsen, J. Alloys Comp. 289 (1999)
197
- 25 14. "Lithium-beryllium hydrides: the lightest reversible metal hydrides" A.
Zaluska, L. Zaluski and J.O. Ström-Olsen, J. Alloys Comp. 307 (2000)
157-166.

- 17 -

CLAIMS

1. A process for generating hydrogen from a metal hydride comprising:
reacting a metal hydride with at least one alcohol.
- 5 2. A process according to claim 1, wherein said at least one alcohol is of
formula ROH in which R is an alkyl group of 1 to 10 carbon atoms.
3. A process according to claim 2, wherein R is an alkyl group of 1 to 6
carbon atoms.
- 10 4. A process according to claim 2, wherein R is an alkyl group of 1 to 4
carbon atoms.
5. A process according to claim 1, 2, 3 or 4, wherein said at least one
alcohol is an aqueous alcohol.
- 15 6. A process according to any one of claims 1 to 4, wherein said at least one
alcohol comprises a mixture of two or more alcohols.
- 20 7. A process according to any one of claims 1 to 6, wherein said metal
hydride is a simple metal hydride.
8. A process according to claim 7, wherein said simple hydride is of a metal
selected from the group consisting of Li, Na, K, Mg, Ca, Zr and Ti.
- 25 9. A process according to any one of claims 1 to 6, wherein said metal
hydride is a complex metal hydride.
10. A process according to claim 9, wherein said complex hydride is
30 represented by the formula:



in which

- 18 -

M^2 is a metal selected from the group consisting of Li, Na, K, Mg, Ca, Fe and Zr;

M^3 is selected from the group consisting of Al, B, Be and Ti;

v is an integer of 1 to 3;

5 w is an integer of 1 to 3; and

y is an integer of 4 to 8.

11. A process according to any one of claims 1 to 10, wherein said metal hydride is contained in a first housing and said at least one alcohol is housed in a 10 second housing, and wherein said at least one alcohol is fed from said second housing to said first housing and reacts with said metal hydride in said first housing, and recovering generated hydrogen from said first housing.

12. A hydrogen generator comprising:

15 a) a first housing containing a metal hydride;

b) a second housing containing at least one alcohol for reaction with said metal hydride;

c) flow means for delivery of said at least one alcohol from said second housing to said first housing; and

20 d) hydrogen gas outlet means in said first housing for delivery of generated hydrogen gas from said first housing.

13. A generator according to claim 12, wherein said flow means includes control means for controlled delivery of said at least one alcohol from said 25 second housing to said first housing.

14. A generator according to claim 12 or 13, wherein said hydrogen gas outlet means includes control means for controlling delivery of the generated hydrogen gas from the first housing.

30

15. A generator according to claim 11, 12, 13 or 14, wherein said at least one alcohol is of formula ROH in which R is an alkyl group of 1 to 10 carbon atoms.

- 19 -

16. A generator according to claim 15, wherein R is an alkyl group of 1 to 6 carbon atoms.

5 17. A generator according to claim 15, wherein R is an alkyl group of 1 to 4 carbon atoms.

18. A generator according to any one of claims 11 to 17, wherein said at least one alcohol is an aqueous alcohol.

10 19. A generator according to any one of claims 11 to 18, wherein said at least one alcohol comprises a mixture of two or more alcohols.

15 20. A generator according to any one of claims 11 to 19, wherein said metal hydride is a simple metal hydride.

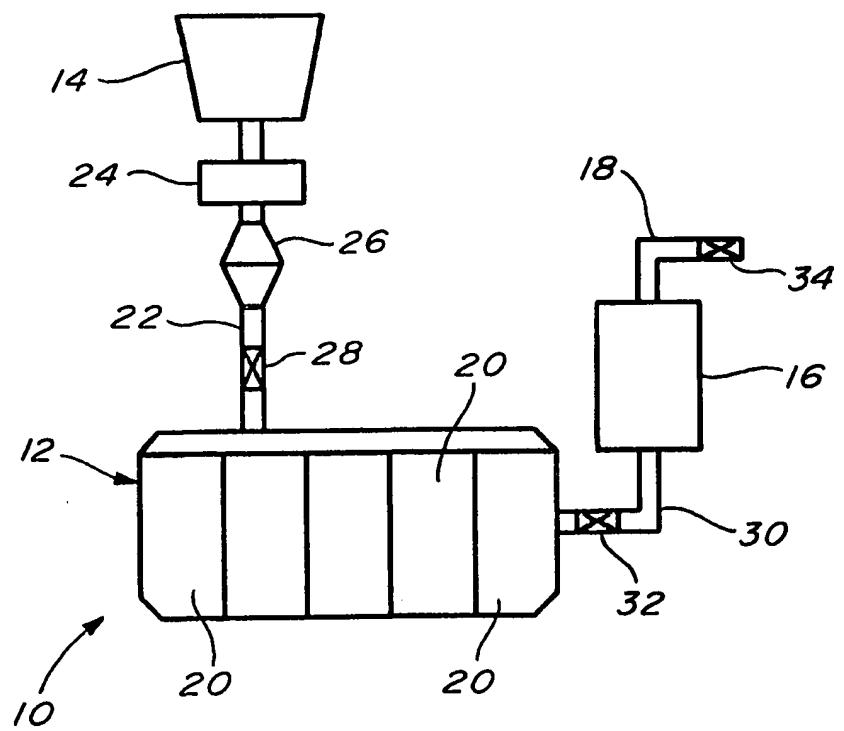
21. A generator according to claim 20, wherein said simple hydride is of a metal selected from the group consisting of Li, K, Na, Mg, Ca, Zr and Ti.

20 22. A generator according to any one of claims 11 to 19, wherein said metal hydride is a complex metal hydride.

23. A generator according to claim 22, wherein said complex hydride is represented by the formula:

25 $M^2_v M^3_w H_y$
in which
 M^2 is a metal selected from the group consisting of Li, Na, K, Mg, Ca, Fe and Zr;
 M^3 is selected from the group consisting of Al, B, Be and Ti;
30 v is an integer of 1 to 3;
 w is an integer of 1 to 3; and
 y is an integer of 4 to 8.

111

FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 01/00682

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B3/06 B01J7/02 B01J8/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B C07F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 115 406 A (MCNEILAB INC) 8 August 1984 (1984-08-08) page 3, line 25 - line 32 ----	1-4,7,8
X	GB 1 189 512 A (CESKOSLOVENSKA AKADEMIE VED) 29 April 1970 (1970-04-29) page 1 -page 2 ----	1-4,8-10
A	US 5 593 640 A (LONG EUGENE ET AL) 14 January 1997 (1997-01-14) claims ----	1,12
A	US 4 155 712 A (TASCHEK WALTER G) 22 May 1979 (1979-05-22) claims -----	1,12

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

T later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

22 August 2001

29/08/2001

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van der Poel, W

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 01/00682

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0115406	A 08-08-1984	US 4499294	A	12-02-1985
		AT 23156	T	15-11-1986
		AU 556591	B	13-11-1986
		AU 2366984	A	26-07-1984
		CA 1196000	A	29-10-1985
		DE 3461089	D	04-12-1986
		HU 190224	B	28-08-1986
		JP 4052272	B	21-08-1992
		JP 59137478	A	07-08-1984
		KR 9100239	B	23-01-1991
		PH 19280	A	04-03-1986
GB 1189512	A 29-04-1970	NONE		
US 5593640	A 14-01-1997	US	5702491	A 30-12-1997
US 4155712	A 22-05-1979	NONE		